Fire performance assessment of FRP materials

Tuula Hakkarainen
Risk and Asset Management
VTT Technical Research Centre of Finland Ltd
Espoo, Finland
tuula.hakkarainen@vtt.fi

Antti Paajanen
Material Modeling and Ecodesign
VTT Technical Research Centre of Finland Ltd
Espoo, Finland
antti.paajanen@vtt.fi

Keywords: fire tests, cone calorimeter, fibre reinforced polymers, resin systems, shipbuilding

ABSTRACT

The European FIBRESHIP research project aims to develop a comprehensive set of methods that would enable the building of the complete hull and superstructure of over 50-metre-long ships in fibre reinforced polymer (FRP) materials. In the work package dedicated to materials selection, an extensive experimental campaign is performed to characterize the fatigue and fire performance of a range of FRP materials and solutions. In this paper, the cone calorimetry results of FRP laminates are introduced in terms of ignitability, heat release, smoke production and effective heat of combustion.

The fire performance of FRP materials can be considerably improved by suitable intumescent coatings. Coatings can significantly change the shape of the heat release and smoke production rate curves, and reduce their maximum values.

Even though fire performance is of high importance in the use of FRP materials, also other properties, such as mechanical properties and manufacturing, need to be taken into account. In some cases, products with excellent fire performance have to be discarded from further considerations due to other issues.

INTRODUCTION

Today, fibre reinforced polymer (FRP) materials are extensively used for building lightweight hull structures of vessels with length up to about 50 metres, whereas in longer vessels their use is limited to secondary structures and components. In the European FIBRESHIP research project [1], innovative FRP materials are evaluated, new design and production procedures and guidelines are elaborated, and new validated software analysis tools are developed. As a result of the project, a comprehensive set of methods will be compiled, enabling the building of the complete hull and superstructure of over 50-metre-long ships in FRP materials. The results enhance significantly the use of FRP materials in shipbuilding and strengthen the competitiveness of the European shipbuilding industry on the world market.

In the work package dedicated to materials selection, an extensive experimental campaign is performed in two phases to characterize the fatigue and fire performance of FRP materials and solutions. For the first phase, seven commercially available resin systems representing different resin classes (see Table 1) were chosen for initial screening. The fire performance of the candidate resin systems was evaluated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) for cured resins, and by cone calorimeter tests for composite laminates with glass fibre reinforcement. This paper concentrates on the cone calorimeter test results obtained in the first phase, describing the ignition propensity and heat release and smoke production characteristics of the laminates. The data produced serves for the evaluation and selection of resin systems for the second phase.

EXPERIMENTAL

Composite laminates with glass fibre reinforcement were manufactured by vacuum assisted resin transfer moulding. The laminates were 500 mm wide and 350 mm in length (fibre direction), and specimens of appropriate size were extracted for testing the mechanical properties and fire performance. The thickness of the laminates was ca. 3 mm.

The cone calorimeter tests were performed in two replicates in horizontal orientation at an irradiance level of 50 kW/m^2. Before the tests, the specimens were conditioned to constant mass in the temperature of (23 ± 2) ◦C and the relative humidity of (50 ± 5) % RH.

The measurement uncertainty of the cone calorimeter test method has been studied in detail e.g. by Enright & Fleischmann [2] and Zhao [3]. According to their studies, the measurement uncertainty of the heat release rate per unit area (HRR) in the range of 100–500 kW/m^2 is of the order of 6% [2] or 10–35% [3], lower HRR values having higher uncertainties. Since the maximum values of heat release rate per unit area (HRR_{max}) in this test series were mostly in the range of 250 kW/m^2 or more, their measurement uncertainty can be considered to be typically in the range of 6–15%.

The repeatability of the results in this test series appeared to be good as shown by Table 1 and Figure 1.

RESULTS AND DISCUSSION

The results of the cone calorimeter tests are presented in Table 1 and Figure 1.

Cellobond J2027X showed the best fire performance in terms of both time to ignition, heat release and smoke production. Its ignition behaviour was exceptional and differed clearly from other specimens: first, a small local flame appeared close to the spark igniter, and then the flames spread gradually over the specimen surface.

The specimens based on epoxy or bio-epoxy resin, i.e. Prime 27, SR1125 without topcoat and Super Sap, behaved rather similarly. The times to ignition were relatively long, but heat release and smoke production were high.

Crestapol 1210 showed intermediate results in terms of time to ignition, heat release and smoke production. LEO system without a topcoat exhibited results comparable to Crestapol 1210, with the exception of higher smoke production.

Elium had the shortest time to ignition. Its maximum heat release rate was intermediate but the total heat release was high. The smoke production was low. The combustible material of Elium specimens was completely consumed during the tests, only glass fibres remaining.

The measured effective heats of combustion were in the range of 19−23 MJ/kg for all composite laminates tested.

Two of the composite laminates, LEO system and SR1125, were tested both with and without an intumescent topcoat. The coating had a significant influence on the fire performance, as seen in Figs. 1a and 1d. In the case of LEO system, the time to ignition increased from 50 to 75 seconds in average due to the coating. A notable change was seen in the shape of heat release rate and smoke production rate curves. For the coated LEO system specimens, the curves were rather flat on a very low level. In the case of SR1125, the coated specimens exhibited two maxima and an intermediate plateau. The times to ignition of coated and uncoated SR1125 specimens were similar. For both LEO system and SR1125, the total heat release values were of the same order for coated and uncoated specimens, but the total smoke production was reduced due to the coating.

The potential of the laminates manufactured using the candidate resin systems to meet the criteria of the IMO FTP Code Part 5 test [4] can be estimated on the basis of cone calorimeter test results at the irradiance of 50 kW/m^2 as presented in [5]. The surface flammability criteria of IMO FTP Code Part 5 test are summarized in Table 2. Taking into account the criteria for critical flux at extinguishment (CFE), the maximum area that can burn to still meet the criteria can be estimated. Figure 2 illustrates the estimation of maximum burning surface area using the criteria for bulkhead, wall and ceiling linings as an example: to meet the criterion of CFE $\geq$ 20 kW/m^2, the maximum burning area is ca. 0.053 m^2. Taking into account the heat release (Q_p) limit of 4 kW and the total heat release (Q_t) limit of 0.7 MJ, estimates for a product fulfilling low flame spread criteria can be formed. Using the described assessment combined with expert assessment based on practical experience, the following results in cone calorimeter tests at 50 kW/m^2 can be used as estimates for the potential of a product fulfilling surface flammability criteria:

- bulkhead, wall and ceiling linings:
  - maximum heat release rate $\leq$ 80 kW/m^2
  - total heat release $\leq$ 13 MJ/m^2
  - time to ignition at least about 40 s
- floor coverings:
  - maximum heat release rate $\leq$ 150 kW/m^2
  - total heat release $\leq$ 27 MJ/m^2

In all cases, the heat of combustion of the product in the thickness used should be $\leq$ 45 MJ/m^2. More details on the estimation can be found in [5]. It is noted that this assessment procedure results in rule-of-thumb estimates for product development purposes. It is noted that the estimates are conservative, since the flame front in the IMO FTP Code Part 5 test does not necessarily proceed evenly over the whole width of the specimen. Thus, the actual surface area burning can be smaller than the maximum area estimate, allowing somewhat higher maximum heat release rate and total heat release values than stated above.

On the basis of the estimation above, the phenolic resin based Cellobond J2027X shows the best potential to meet the surface flammability criteria of IMO FTP Code Part 5 test. Also LEO system with topcoat appears to be promising, even though its total heat release exceeds the limit of this estimation.

In the selection of resin systems for the second phase, fire performance was not the only criterion, even though it can be considered to be one of the main issues in the use of FRP materials in large-length ships. Property classes taken into account in the selection were mechanical properties (including interlaminar shear strength, flexural strength, and flexural stiffness), manufacturing (including elevated temperature infusion and/or cure requirement, elevated temperature post-cure requirement, infusion capability, and worldwide awareness), and impact (including cost, fire retardancy, worker health impact, and recyclability). The weights given to these property classes were 20 points for mechanical properties, 50 points for manufacturing, and 40 points for impact. The division of weight points to different properties is shown in Table 3. Regarding manufacturing, the need of heat in the curing process was seen as a possible reason to eliminate a material candidate. Infusion properties were considered to be one of the most important factors: if the material is very difficult to infuse, it can lead to a poor quality of the manufactured part, making it useless. Regarding impact, the most important aspects were seen to be fire retardancy and the cost.

Considering the various aspects, LEO system and SR1125, both with the topcoat, were selected for the second phase. Cellobond J2027X, showing the best fire performance, was discarded due to its elevated temperature infusion, cure and post-cure requirements, and the high infusion temperature required.

SUMMARY AND CONCLUSIONS

The fire performance of seven commercially available resin systems was studied by performing cone calorimeter tests of glass fibre reinforced composite laminates at the irradiance of 50 kW/m^2. As a result, data on the ignitability, heat release, smoke production and effective heat of combustion of FRP materials based on different resin classes was obtained.

The best fire performance was exhibited by the laminate based on phenolic resin in terms of both time to ignition, heat release, and smoke production.

The fire performance of FRP materials can be considerably improved by suitable intumescent coatings. In this test series, coatings could significantly change the shape of heat release rate and smoke production rate curves and reduce their maximum values. The coatings reduced total smoke production but had no significant effect on total heat release. In one case, time to ignition was increased by 50 % due to the coating.

The potential of a product to meet the criteria of the IMO FTP Code Part 5 test can be estimated on the basis of cone calorimeter tests at the irradiance of 50 kW/m^2. It is noted, however, that the estimation is indicative: the estimation procedure has been put on the safe side and a product can pass Part 5 even though all cone calorimeter test results would not refer to that.

Even though fire performance is an important issue in the use of FRP materials, also other properties must be taken into account. This includes at least mechanical properties, manufacturing aspects, and the cost.

ACKNOWLEDGEMENTS

The Irish Composites Centre of University of Limerick is gratefully acknowledged for manufacturing the composite laminate specimens for the tests.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 723360.

REFERENCES

[1] www.fibreship.eu

[2] P. Enright, C. Fleischmann, Uncertainty of heat release rate calculation of the ISO5660-1 cone calorimeter standard test method, Fire Technology 35 (2) (1999) 153–169.

[3] L. Zhao, Bench Scale Apparatus Measurement Uncertainty and Uncertainty Effects on Measurement of Fire Characteristics of Material Systems (MSc thesis), Worcester Polytechnic Institute, 2005, 185 p.

[4] IMO 2010 FTP Code Part 5 – Test for surface flammability (Test for surface materials and primary deck coverings).

[5] T. Hakkarainen, J. Hietaniemi, S. Hostikka, T. Karhula, T. Kling, J. Mangs, E. Mikkola, and T. Oksanen. Survivability of ships in case of fire − Final report of SURSHIP-FIRE project. Espoo: Technical Research Centre of Finland, 2009. 120 p. + app. 7 p. (VTT Research Notes 2497.) https://www.vtt.fi/inf/pdf/tiedotteet/2009/T2497.pdf

Table 1. Cone calorimeter test results of composite laminates. Abbreviations: t_{ig} = time to ignition; HRR_{max} = maximum heat release rate; THR = total heat release; TSP = total smoke production; $\Delta H_{c,\,eff}$ = effective heat of combustion.

Resin class	**Resin details**		**t_{ig} (s)**	**HRR_{max} (kW/m^2)**	**THR (MJ/m^2)**	**TSP (m^2)**	**$\Delta H_{c,\,eff}$ (MJ/kg)**
Vinylester	LEO system without topcoat	Test 1	53	330	36.0	16.0	20.6
		Test 2	47	341	31.0	14.2	20.3
		Average	**50**	**336**	**33.5**	**15.1**	**20.4**
	LEO system with topcoat	Test 1	75	69	42.2	8.5	19.6
		Test 2	74	68	42.3	9.1	19.6
		Average	**75**	**69**	**42.3**	**8.8**	**19.6**
Urethane acrylate	Crestapol 1210	Test 1	43	320	36.2	9.7	20.8
		Test 2	44	308	34.6	9.0	20.6
		Average	**44**	**314**	**35.4**	**9.3**	**20.7**
Epoxy	Prime 27	Test 1	60	494	40.1	10.9	22.1
		Test 2	59	498	38.7	10.5	21.6
		Average	**60**	**496**	**39.4**	**10.7**	**21.9**
Epoxy	SR1125 without topcoat	Test 1	50	507	43.8	13.9	21.1
		Test 2	55	585	41.1	13.0	21.0
		Average	**53**	**546**	**42.5**	**13.5**	**21.1**
	SR1125 with SGi 128 topcoat	Test 1	50	267	43.7	9.6	21.6
		Test 2	53	255	37.6	9.0	20.8
		Average	**52**	**261**	**40.7**	**9.3**	**21.2**
Bio-epoxy	Super Sap CLR	Test 1	60	498	41.2	11.9	22.3
		Test 2	62	541	42.7	12.1	23.6
		Average	**61**	**520**	**42.0**	**12.0**	**23.0**
Phenolic	Cellobond J2027X	Test 1	86 *)	74	9.9	0.4	19.3
		Test 2	115 *)	67	9.9	0.3	19.0
		Average	**101** *)	**71**	**9.9**	**0.4**	**19.1**
Thermoplastic	Elium	Test 1	23	251	41.2	1.8	22.7
		Test 2	22	258	40.1	1.8	23.0
		Average	**23**	**255**	**40.7**	**1.8**	**22.9**

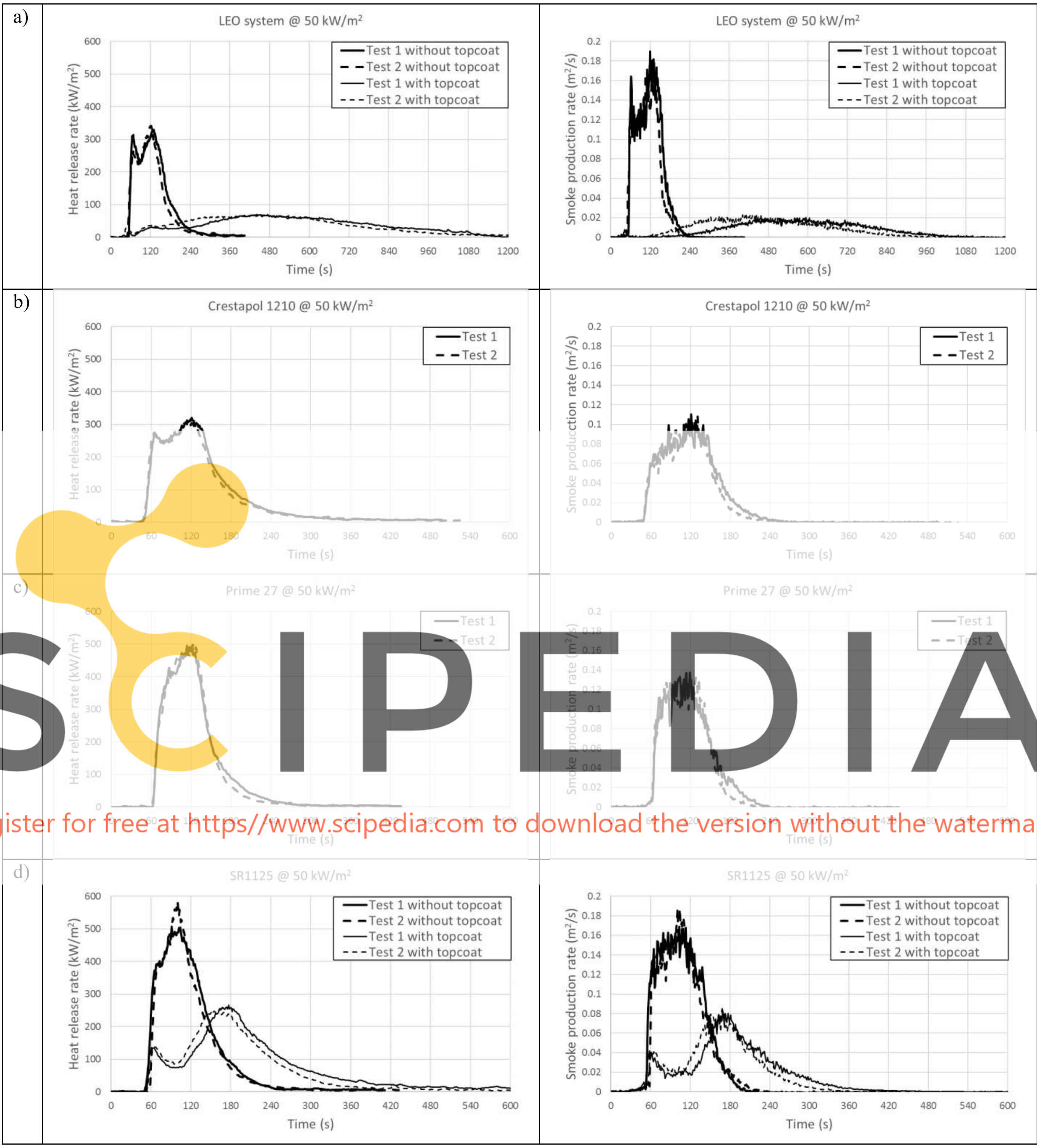
*) The first flame of sustained flaming, close to the spark igniter. The flames spread gradually over the whole specimen surface.

Table 2. Surface flammability criteria in IMO FTP Code Part 5 test [4]. Abbreviations: CFE = critical flux at extinguishment; Q_{sb} = heat for sustained burning; Q_t = total heat release; Q_p = peak heat release.

Quantity	**Floor coverings**	**Bulkhead, wall and ceiling linings**
CFE (kW/m^2)	$\geq$ 7.0	$\geq$ 20.0
Q_{sb} (MJ/m^2)	$\geq$ 0.25	$\geq$ 1.5
Q_t (MJ)	$\leq$ 2.0	$\leq$ 0.7
Q_p (kW)	$\leq$ 10.0	$\leq$ 4.0

Table 3. Weight points of different properties in the selection of resin systems for the second phase.

Property class	Property	Weight points
Mechanical properties	Interlaminar shear strength	10
	Flexural strength	5
	Flexular stiffness	5
Manufacturing	Elevated temperature infusion and/or cure requirement	10
	Elevated temperature post-cure requirement	10
	Infusion capability	20
	Worldwide awareness (i.e. well known and easily available)	10
Impact	Cost	15
	Fire retardancy	21
	Worker health impact	2
	Recyclability	2


a)
LEO system @ 50 kW/m²
Heat release rate (kW/m²)
Smoke production rate (m²/s)
Time (s)
Test 1 without topcoat
Test 2 without topcoat
Test 1 with topcoat
Test 2 with topcoat
b)
Crestapol 1210 @ 50 kW/m²
Heat release rate (kW/m²)
Smoke production rate (m²/s)
Time (s)
Test 1
Test 2
c)
Prime 27 @ 50 kW/m²
Heat release rate (kW/m²)
Smoke production rate (m²/s)
Time (s)
Test 1
Test 2
d)
SR1125 @ 50 kW/m²
Heat release rate (kW/m²)
Smoke production rate (m²/s)
Time (s)
Test 1 without topcoat
Test 2 without topcoat
Test 1 with topcoat
Test 2 with topcoat

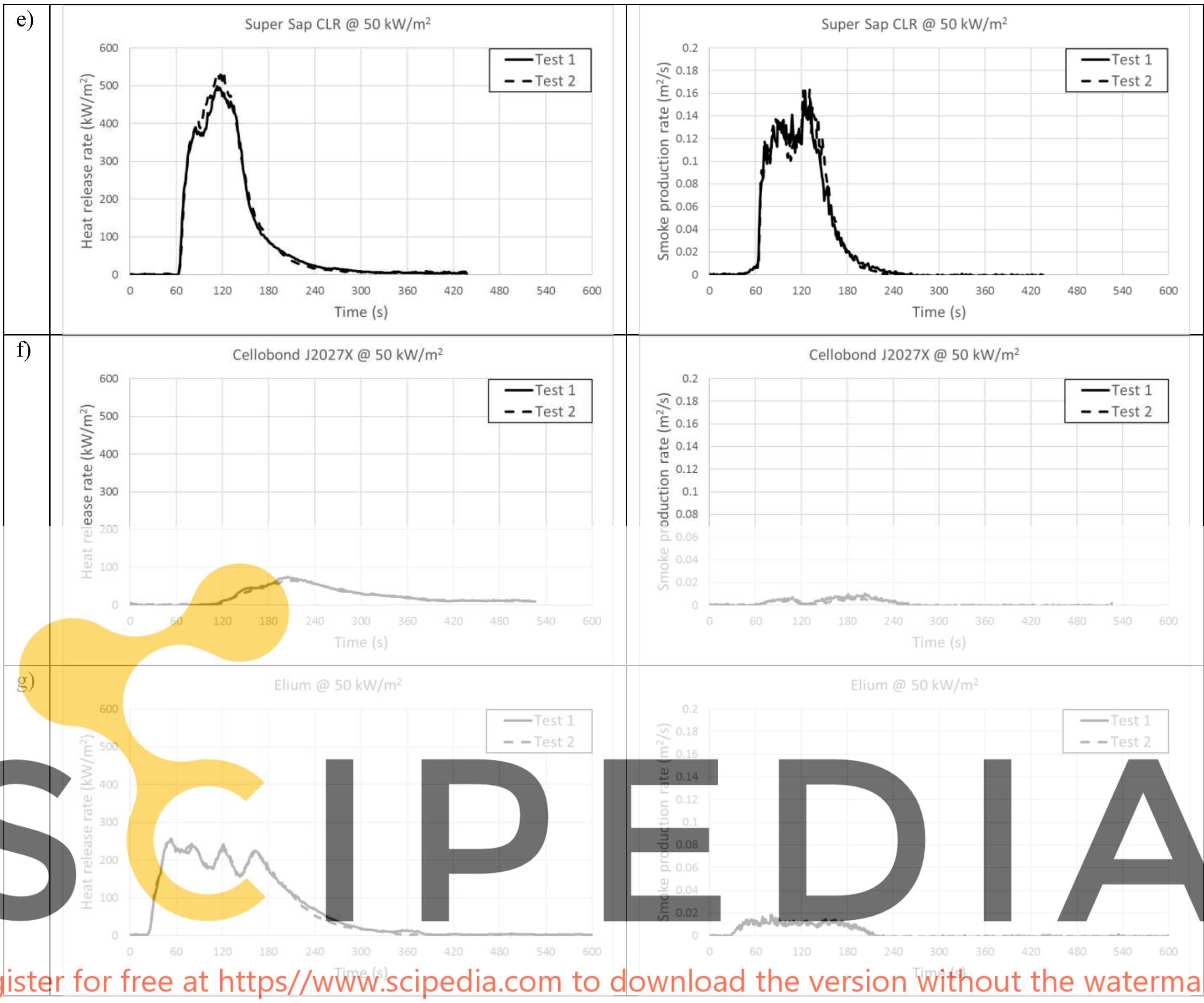


Figure 1. Heat release rate (left) and smoke production rate (right) results of composite laminates in cone calorimeter tests with an irradiance of 50 kW/m²: a) LEO system with and without a topcoat, b) Crestapol 1210, c) Prime 27, d) SR1125 with and without a topcoat, e) Super Sap CLR, f) Cellobond J2027X, and g) Elium. Note that the time scale of LEO system graphs is double compared to other graphs.

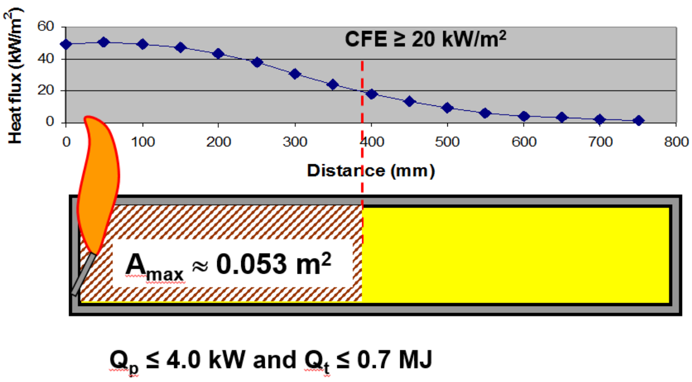


Figure 2. Estimation of maximum burning surface area for meeting the criteria for bulkhead, wall and ceiling linings in IMO FTP Code Part 5 test.